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MECHANICAL REINFORCEMENT OF BIOGLASS®-BASED SCAFFOLDS

Field: Physical and materials engineering

Supervisor: Prof. Ing. Ivo Dlouhý, CSc.
KEYWORDS
Bioactive glass, scaffolds, composite material, mechanical properties, tensile test, SPS.

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1. Introduction

Materials science is facing since decades the challenge of developing advanced and multifunctional biomaterials able to substitute, permanently or temporary the damaged parts. In the case of bone tissue engineering, such materials are required when a section of bone is missing and the gap needs to be filled in, for instance following an accident or after the removal of a tumor. A suitable alternative is offered by tissue engineering (TE), whose aim is to regenerate damaged tissues, instead of replacing them, by developing artificial biological substitutes that restore, maintain or improve tissue function [1]. From this standpoint, it can be stated that the main aim of bone TE is to restore and maintain the function of human bone tissues. To accomplish such demanding task, three-dimensional resorbable porous structures, able to trigger the formation of living tissue are required. Their surface should allow cells to attach, proliferate and differentiate [2]. Specialized scientific literature termed these structures as “scaffolds”. During the last 20 years, ceramics started to be widely used in medical applications. According to their interaction with the surrounding living tissue, they can be classified in four categories [3]:

- **Nearly inert** whose fixation take place by mechanical interaction or morphological fixation (e.g. alumina and zirconia femoral heads);
- **Porous** whose fixation is due biological ingrowth into implant pores (e.g. hydroxyapatite (HA) and HA–coated porous metals used for femoral stems);
- **Bioactive** for which the fixation occurs by chemical bonding with implant and tissues (e.g. bioactive glasses (BGs) used for dental and orthopaedic devices);
- **Resorbable** as the the fixation occurs through replacement of the implant by living tissue.

Manmade materials (alloplastic or synthetic bone grafts) stand out as a reasonable option, because they are easily available and might be processed and modified to suit the specific needs of a given application [4]. What’s more, there are no concerns about potential infections, immunological incompatibility, sterility or donor site morbidity. Therefore investigations on artificial materials for bone tissue repair appear to be one of the key subjects in the field of biomaterials research for clinical applications. Nevertheless, the key-problem is that mechanically strong materials are usually bioinert, while bioresorbable and degradable materials are in general mechanically weak [5]. Therefore, a methodology which enables the production of BGs-based scaffolds with superior mechanical properties has to be developed.

In 1969, Hench and co-workers discovered that certain silica based glasses can chemically bond to bone. It was later elucidated that this process is the result of a sequence of reactions involving ionic exchange for the glass surface wetted by biological fluids which lead to the formation of a hydroxy carbonate apatite (HCA) layer. More specifically, the processes on the glass surface are characterized by ion leaching/exchange, dissolution of the glass network and precipitation and growth of a calcium-deficient HCA layer, whereas cellular reactions include colonization, proliferation and differentiation of relevant bone cells [6]. Further studies led to the establishment of a silica-based bioactive glass named as 45S5 Bioglass® having the following composition: 45 wt % SiO₂, 24.5 wt % Na₂O, 24.5 wt % CaO and 6 wt % P₂O₅. Its
atomic structure can be visualized as a collection of silica tetrahedra connected by –Si–O–Si–
bridging oxygen bonds.

One of the biggest difficulties in the production of porous bioactive scaffolds from sintering of Bioglass® powders, it is due that the crystallization of different phases, which hinder the densification process and resulting in mechanically poor scaffolds. The combination of softer synthetic polymers and stiff inorganic materials such as glasses and ceramics has been attempted in order to obtain scaffolds which somehow mimic the structure of living bone [7]. Bone in fact is a composite material itself, composed of carbonated apatite (65 dry wt. %) which confers structural reinforcement and collagen (35 dry wt. %) which contributes to an increase of flexibility and toughness. The deposition of a thin polymeric coating on bioactive ceramic/glass scaffolds in order to increase their strength and crack resistance is an effective method which has been already reported by several researchers. Ideally, composites should provide enhanced mechanical performances and obtain properties that are unavailable from the individual constituent materials.

2. Theoretical background

Bioglass®-based scaffolds produced by foam replication can be classified as open-cell reticulated brittle foams according to their three-dimensional morphology. What has been clearly assessed is that four factors mainly influence the mechanical response of ceramic foams [8]:

1. The topology (connectivity) and shape of the cells.
2. The properties of the solid of which the foam is made.
3. The relative density $\rho_f/\rho_s$ of the foam, where $\rho_f$ is the density of the foam and $\rho_s$ that of the solid of which it is made.
4. The amount and type of defects depending on process used.

For optimizing the fabrication of Bioglass® scaffolds it is crucial to understand the phase transformations and thermodynamics and kinetics processes which occur during the sintering. Several studies have been conducted with the aim of investigate this aspects. In this way, the heating treatment can be tailored in order to achieve the highest density either of a bulk Bioglass® piece or of the struts constituting porous open-cell foams. Sintering of glass particles occurs by viscous flow and this process is hindered as crystallization starts [9]. During heating of Bioglass® particles at constant rate, five structural transformations and three main steps of densification were detected by differential thermal analysis (DTA) [10]–[12]. The first densification step occurs between 550 and 620 °C, in correspondence of the first glass transition ($T_{g1}$). Around 570 °C, a glass-in-glass transition takes places ($T_s$). Between 620 and 675 °C, minor second step of densification is observed. This domain corresponds to the crystallization of the $\text{Na}_2\text{CaSi}_2\text{O}_6$ from the silica-rich phase ($T_{c1}$) [11]. The sintering process stops at 850 °C. At this temperature, a third step of shrinkage begins, due to the second glass transition ($T_{g2}$) and at 1000 °C a density of 85% is obtained. At 1100 °C, the
maximum density is achieved. By increasing further the temperature up to 1200 °C, melting occurs.

![Graph showing temperature transitions](image)

**Fig. 1a** Influence of heating rate on the shrinkage of the powders compact and **b)** on the gap $T_{g1} - T_s$ [9].

Lefebvre et al. [11] reported a significant increase in the first step of shrinkage due to viscous flow with increasing heating rate. This can be properly seen in the inset of the Fig. 1a, which was obtained for a larger set of data [9]. Despite the high variability of the results, a tendency towards an increase in the first linear shrinkage is observed when the heating rate increases. This phenomenon was quantified in terms of shrinkage of a compact of powder and the variation of gap between $T_{g1}$ and $T_s$ with different heating rates (Fig. 3b). Thus, a faster heating rate leads to a larger temperature range where the viscous flow is not influenced by the structural transformation of Bioglass®. From this perspective, spark plasma sintering (SPS) technique could be interesting since it open the possibility to achieve much higher heating rates in comparison with traditional techniques.

Foam-replication is a simple technique which enables the production of open cell ceramic foam with controlled macroporosity [13]. The process consists of dipping an open–cell polymeric foam into a ceramic slurry. After dipping, samples are squeezed in order to remove the excessive slurry and the resulting green body is subsequently dried. The burning of template and sintering can be carried out in a single step. The most used templates for this application are reticulated polyurethane (PU) foams. The final result is a ceramic foam distinguished by a reticulated structure (>85% of total porosity) and hollow struts resulting from the burning out of the polymer foam substrate. Lower mechanical properties and large defect population are therefore a typical characteristic of this route. Dipping can be repeated several times in order to achieve the desired coating thickness, which will in turn determine the cross–sectional area of the struts in the sintered foam. In 2006, Chen et al. [14] fabricated for the first time a three-dimensional, highly porous Bioglass®-based scaffold by foam replication process, using melt-derived 45S5 Bioglass® powder. The steps involved in replica
process and the thermal profile they used for sintering are summarized in Fig. 2. Nearly full densification of the struts occurred and fine crystals of Na$_2$Ca$_2$Si$_3$O$_9$ (Combeite) were detected.

![Flow chart](image)

**Fig. 2a) Flow chart of the foam replication process used to the production of Bioglass®-based scaffolds and b) conventional heat treatment program designed for the sintering of 45S5 Bioglass® scaffolds [14].**

The properties of sintered 45S5 BG can in be widely scattered, depending on the amount of crystalline phase in the amorphous matrix, which can be in turn controlled by tailoring the thermal treatment used for sintering. It is in fact well known that glasses can be strengthened by the formation of crystalline domains in the glass matrix upon heat treatment [15, 16]. Glass-ceramics with crystalline volume fraction between 34 and 60% exhibited improvement of three times in fracture strength and an increase of 40% in indentation fracture toughness compared with the parent glass. In numerous papers dealing with dense and porous 45S5 Bioglass®, the effect of crystalline volume fraction (at constant crystal size) and crystal size (at constant crystallized volume fraction) was investigated [14], [17]–[20]. These results demonstrated that it is possible to design bioactive glass-ceramics with improved microstructures by finely tuning the sintering process. Some values related to mechanical properties of amorphous Bioglass® are reported in Tab. 1. According to Peitl et al. [21], the introduction of crystallinity in this bioactive glass significantly increased the fracture strength from 80 to 210 MPa and the indentation toughness from 0.60 to 0.95 MPa·m$^{1/2}$, while the Young modulus underwent only a small increase from 60 to 70 GPa. These overall improvements in mechanical properties were attributed to crack deflection mechanisms within the material.
<table>
<thead>
<tr>
<th>Material property</th>
<th>Trabecular bone [MPa]</th>
<th>Cortical bone [MPa]</th>
<th>Bioglass® (bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength</td>
<td>0.1 – 16 [77, 78]</td>
<td>130 – 200 [77, 79]</td>
<td>500 [24]</td>
</tr>
<tr>
<td>Compressive modulus</td>
<td>0.12 – 1.1 [80, 81]</td>
<td>11.5 – 17 [28]</td>
<td>n. a.</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>0.05 – 0.5 [74, 79]</td>
<td>7 – 30 [74, 79]</td>
<td>35 [25]</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>n. a.</td>
<td>2 – 12 [73, 79]</td>
<td>0.7 – 1.1 [30]</td>
</tr>
</tbody>
</table>

Tab. 1. Bioglass® mechanical properties summarized by Gerhardt et al. [31].

Several models have been developed to correlate the mechanical properties of open cell ceramics foams (Young’s modulus, Poisson’s ratio, fracture toughness, tensile strength and compressive strength) of ceramic foams to their topology and micro-structural features [8], [32]–[35]. A micromechanical model often used to predict properties such as elastic modulus and crushing strength of porous Bioglass scaffolds is the Gibson-Ashby (GA) model [8]. This model was the result of the research endeavors of Gibson [36] and Green [37] and it is based on the simplification of a given body structure to a more uniform and idealized one. GA model idealizes them as sequence of cubic cells, whose repetitive unit is shown in Fig. 3b. The struts are in this case idealized as rigid defect-free beams, having theoretical density. In the linear elastic regime, under uniaxial stress, open-cell foams deform primarily by bending of the cell edges. It has been assayed that the compressive response of Bioglass®-based foams is characterized by linear elasticity at low stresses followed by an extended collapse plateau and a period of densification in which the stiffness increases sharply. As a force $F$ is acting on the cell as shown in Fig. 3b, the Young’s modulus of the foam and its brittle collapse stress $\sigma^*_{cr}$ is given by [38]:

$$E^* = E_s C_1 \left( \frac{\rho_f}{\rho_s} \right)^2,$$  \hspace{1cm} (1)

$$\sigma^*_{cr} = \sigma_{fs} C_2 \left( \frac{\rho_f}{\rho_s} \right)^{3/2},$$  \hspace{1cm} (2)

where $E_s$ is the Young’s modulus of the solid and $\sigma_{fs}$ is the modulus of rupture of the strut material. $C_1$ and $C_2$ are geometrical constants of proportionality. By fitting the experimental data, were found to be 0.3 and 0.65 respectively [38], [39]. Nevertheless, due to the reduced magnitude of displacements in the elastic region, acquired data are not always reliable.
Even though this represents an idealized structure far from the reality, it emphasizes the bending of struts under axial loads. For a low density material \( (\rho / \rho_s < 0.1) \) it has been found to be \( \rho / \rho_s \sim (t/L)^2 \). By reviewing the literature on this topic, it can be found that different polymers, either natural or synthetic have been used for this purpose. Among the natural ones, collagen [41], alginate [42], silk [43], gelatin [44] and chitosan [45] can be mentioned. Concerning the synthetic ones, poly(lactic acid) [46], poly(hydroxybutyrate) [47], PHBV [48], poly(ɛ-caprolactone) [49] were reported as well. Besides sufficient mechanical capability, coatings for bone replacement scaffolds must also fulfill other requirements such as biocompatibility, biodegradability and tunable degradation rate. The addition of polymer completely changes the mechanical behaviour of the scaffold and the load–deflection curves can now be decomposed in three stages: a linear elastic one in which the maximum stress is reached, a drop of the load and a plateau during which the load remains roughly constant while the deflection can reach several microns depending on the infiltration method and polymer properties. The description of the stress intensity factor for dense, homogeneous, isotropic solids which exhibit linear elastic behavior can readily be described by the well-known relationship [50]:

\[
K_I = \sigma_a Y \sqrt{C},
\]

where \( K_I \) is the stress intensity factor for opening mode I, \( \sigma_a \) is the stress applied to the material at some distance remote from the crack tip, \( Y \) is a dimensionless parameter which depends upon the geometry of the loading and crack configuration and \( C \) is the characteristic dimension of the flaw. In loading a material, once \( K \) reaches a critical value denoted \( K_{IC} \), unstable crack growth occurs. \( K_I \) is typically considered to be an intrinsic material property which may be used to characterize the material's mechanical integrity. Using the theory of elasticity, it is possible to calculate the stress field in the proximity of a crack in an arbitrary body with an arbitrary crack undergoing arbitrary loading.
\[ \sigma_{yy} = \frac{K_f}{\sqrt{2\pi r}} \]  

(4)

where \( r \) is the distance from the crack tip along the x-axis. The fracture toughness, \( K_{IC} \), is the critical value of the stress intensity factor at a crack tip needed to produce unstable catastrophic failure under general triaxial loading.

2.1 Microfibrillated cellulose

Cellulose is a linear, high–molecular-weight hydrophilic polysaccharide consisting of repeating poly-\( \beta \)-(1,4)–D–glucopranose units. Microfibrillated cellulose (MFC) consists of high aspect ratio cellulose nanofibrils obtained either by mechanical disintegration or by acid hydrolysis of the wood cell wall [51]. MFC was first prepared by Herrick et al. and Turbak et al. in 1983, by fibrillating wood pulp by means of a high-pressure homogenizer. Ankerfors et al. [52] established a new processing route, combining the mechanical treatment with chemical or enzyme-based pretreatment which lowers the strength of inter–fibrils interactions. In this way the energy consumption of the process could be decreased, opening up the possibility of large scale production and commercial exploitation. Properties such as non–toxicity, biodegradability, large surface area and remarkably high elastic modulus (~ 146 GPa [53]) make this material a suitable reinforcing agent for biocoatings. The noticeable improvement of PVA films mechanical properties by addition of MFC has been extensively reported in several investigations [51, 54, 55]. One of the most commonly reported technique for the production of MFC-reinforced PVA composite is film casting [55-57].

2.2 Spark plasma sintering

The spark plasma sintering technique has been gaining importance as it allows the achievement of highly dense ceramic compacts with minor grain growth [56]. In the SPS process, a high energy electric spark is discharged and the powder particle surfaces are more easily purified and activated than in conventional sintering process. The presence of spark plasma significantly enhances rapid densification to densities close to the theoretical one [57]. The high heating rates (typically between 100 and 600° C/min) bring the sample rapidly to high temperatures assisting densification mechanisms over non–densification mechanisms [58]. The mechanical compression of the sample is another factor that accelerates the material densification in the SPS method [56]. These peculiarities allow to achieve densities closer to theoretical one at lower sintering temperatures as well as shorter sintering cycles, compared to conventional sintering and hot press techniques. Therefore, SPS offers a well-established technological and economical approach for fabricating net–shaped bioactive glass materials, including Bioglass® matrix composites. Chen et al. [59] reported a successful sintering of sol–gel derived Bioglass® powder by SPS. In particular, it was found that the sol–gel derived Bioglass®-ceramics sintered with the SPS technique at 950 °C for 15 min had a high Young’s modulus value of ~110 GPa, which was comparable to that of compact bone and significantly higher than the maximal value achieved by the conventional heat treatment. Grasso et al.
reported as well the sintering of 45S5 Bioglass® powder by SPS [60]. Temperature and pressures ranging respectively from 350 to 550 °C and 70 to 300 MPa were used. Fully dense and completely amorphous 45S5 Bioglass® samples at temperatures as low as 500–550 °C were obtained.
3. **Aims of the work**

The main aim behind this work is the mechanical improvement of bulk Bioglass® and Bioglass®-based porous scaffolds. For the latter, it has been followed the approach already described in several works, which involves the addition of a polymeric coating on the scaffold’s surface in order to increase strength and the work of fracture of the structure. The novelty which distinguishes the present work is the use of a composite coating, comprised of polyvinyl-alcohol (PVA) and microfibrillated cellulose (MFC), in order to obtain superior reinforcing effect in comparison with neat-polymer coatings commonly reported in literature. It will be determined through computational methods, which factor among the stiffness of the coating material and the extent of coating infiltration into surface cracks is the most effective in terms of reduction of the stress concentration at defect sights. As an experimental counterpart, the rheological properties of the PVA and PVA/MFC aqueous solutions and their wettability towards Bioglass® surface will be investigated. Coated scaffolds with different ratio of PVA/MFC will be fabricated and tested under uniaxial compressive and tensile mode. Outputs from viscosimetry and wettability measurements will constitute a useful tool to better interpret and correlate the outputs from FEM and the experimental results from compressive and tensile test.

The second part of this work is focused on the production of bulk Bioglass® composites samples by spark plasma sintering (SPS) technique. The author’s interest is to experiment the advantages that such technique may offer in comparison with conventional sintering in oven. In particular, one of the primary aims will be to ascertain whether high heating rates (ranging from 100 to 300 °C/min), the application of mechanical pressure and controlled atmosphere, could lead to the achievement of a finer glass/crystalline microstructure or non-equilibrium phases with peculiar properties.

To summarize, the main research activities covered will be:

- Production of scaffolds by using different kind of slurries;
- Coating of scaffolds by different polymers;
- Mechanical testing of bulk Bioglass®;
- Mechanical testing of coated scaffolds (uniaxial compression, tension);
- Microstructural characterization of scaffolds and fractographic analysis by SEM;
- FE modeling of foam’s unit cell and coating effect;
- Production and characterization of bulk Bioglass® by SPS.
4. Materials and methods

4.1. Samples preparation

For the production of Bioglass®-based scaffolds, commercially available bioactive glass powder (45S5 Bioglass® composition: 45 wt.% SiO₂, 24.5 wt.% CaO, 24.5 wt.% Na₂O, 6 wt.% P₂O₅, Schott AG, Germany) having average particle size of 4 μm (d₅₀: (4.0 ± 1.0) μm d₉₅: ≤20 μm) was used. Fully hydrolyzed PVA, d=1.269 g/cm³ (Sigma Aldrich Chemie GmbH, Germany), was either used as binder for slurry and for coating preparation. Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVHB), having average Mₓ = 170,000–250,000, supplied by Sigma Aldrich Chemie GmbH (Germany) was used as binder for ethanol-based slurry. MFC hydrogel having 2% content of fibers was supplied by Borregard (Sarpsborg, Norway). Three kinds of scaffolds were tested produced and tested under tensile and compressive uniaxial load: uncoated, PVA-coated, PVA/5%MFC-coated, and PVA/10%MFC-coated.

Bulk Bioglass® samples were sintered in two different ways: in conventional furnace and by SPS technique. In the first case, the remainder of slurry used for fabrication of scaffolds was poured in a rubber mold having diameter ~ 40 mm and kept drying for 7 days at room temperature. After drying, the green body was sintered at 1050°C for 1h, using a heating rate of 2 °C/min and a cooling rate of 5 °C/min, similarly to the process reported in Ref. [14] (Fig. 5b). The furnace used was HtIndustry (HTH8, s. r. o., Czech Republic). Dense disk-shaped samples were thus obtained, having thickness and diameter equal to 5 and 30 mm, respectively.

SPS facility HPD 25/1, (FCT Systeme, Germany) was used for the production of pure Bioglass® and Bioglass®/BNNSs bulk samples. Different sintering routes were tested, i.e. by extensively varying parameters such as sintering temperature (Tₛ), heating rate (hᵣ), holding time (tₜ), pressure (P) and atmosphere (i.e. argon for pressure–assisted, vacuum for pressureless sintering), in order to establish the optimal conditions for the achievement of a dense and homogeneous microstructure.

4.2. Characterization

Compressive tests of scaffolds were carried out by using an Instron8862 (Instron®, U. S.) uniaxial machine with electromechanical actuator and integrated with BlueHill® software. The cross-head speed was set as 0.5 mm/min and 100 kN load cell was used. Concerning tensile tests, Z050 uniaxial screw-driven load machine (Zwick GmbH, Germany) with 1kN load cell was used applying a cross-head speed of 0.1 mm/min. Compressive and tensile strength values were determined by dividing the maximum force in the loading diagram by the cross-sectional area of the specimen measured after the test.

The elastic modulus of scaffolds was determined by resonance method and by measuring the slope of the elastic region in the compressive stress–strain curves. For each kind, five curves were considered and average slope was calculated.

For bulk samples, Vickers hardness (HV) was determined by Vickers indentations on polished surfaces of the specimen microtester Zwick/Roell ZHU/Z2.5 (Germany). For statistical
reasons, 13 indents were applied on each sample. Speed point of contact, load application and load removal were set respectively as: 0.05 mm/min, 0.125 N/s and 0.01 mm/min. The impressions were measured by SEM. Chevron-notched beam were cut using a diamond wheel having thickness 0.17 mm. The specimens were loaded in three-point bending (span of 8 mm) at a constant cross-head speed of 0.1 mm/min at room temperature. The cross sections sizes 2.5 × 1.6 mm. Load-deflection traces were recorded and the fracture toughness was calculated from the maximum load ($F_{\text{max}}$) and the corresponding minimum value of geometrical compliance function ($Y_{\text{min}}^*$) using the equation [61]:

$$K_{IC} = \frac{F_{\text{max}}}{bd^{1/2}Y_{\text{min}}^*},$$

where $b$ and $d$ are the width and thickness of the beam, respectively. The notch angle and depth ($a_0$) were measured from optical micrographs of fracture surfaces by ImageJ.

5. Main results

5.1 Uncoated and coated Bioglass scaffolds

The structures of scaffolds obtained by ethanol-based slurry and water-based slurry are shown in Fig. 4a, b, respectively. In both case, the porosity of template (45 PPI), the number of dipping, and the slurry solid fraction (30 %) were the same. The distribution of cell sizes and struts diameters was optimally described by a normal function. Mean cells size and struts thickness measured by image analysis of low magnification resulted as 500 µm and 50 µm, respectively. The scaffolds produced by the ethanol-based slurry exhibited higher degree of interconnection and open porosity in comparison to those produced according to Ref. [14]. The lower surface tension of ethanol likely results in a slurry with better wettability towards the PU surface and the unwanted formation of liquid membranes is prevented. The solid fraction was kept low (30% vol.) in order to promote a homogeneous distribution along the template struts. A sufficient amount slurry was therefore obtained by increasing the number of dipping. In Tab. 2, the porosity (vol. %) of coated and coated scaffolds are summarized.
Tab. 2. Average porosity values for non-coated and coated scaffolds.

<table>
<thead>
<tr>
<th></th>
<th>No coating (%)</th>
<th>PVA-coating (%)</th>
<th>PVA/5%MFC (%)</th>
<th>PVA/10%MFC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>92.51 ± 0.50</td>
<td>90.22 ± 0.56</td>
<td>90.38 ± 1.49</td>
<td>91.39 ± 1.59</td>
<td></td>
</tr>
</tbody>
</table>

Four characteristic compressive stress-strain curves for non-coated, PVA-coated, PVA/5%MFC-coated and PVA/10%MFC-coated scaffolds, respectively, are shown in Fig. 5a. First fracture events (most probably struts fracture) are recorded as the applied stress reaches approximately 0.05 MPa. Beyond this point, the deformation proceeds without further increase of load and progressive crushing of all the struts occurs up to the densification stage. The compressive strength for uncoated scaffolds was 0.053 ± 0.010 MPa whereas PVA-coated samples reach an average value of 0.26 ± 0.04 MPa. The addition of 5 wt. % of MFC fibers to the coating lead to a further increase of the compressive strength up to 0.69 ± 0.10 MPa. As the concentration of MFC fibers was doubled to 10 wt%, the compressive strength of scaffolds decreased to 0.37 ± 0.07 MPa. Results are summarized in Fig. 5b. Therefore, further addition of fibers above 5 wt. % seems to have a detrimental effect on the strengthening action of the coating. This behaviour could be ascribed to a less homogenous distribution of the MFC fibers, as their concentration increase. Also the filling of internal and surface struts defects could be worse for 10 wt. % MFC fibrils in PVA matrix comparing to 5 wt. % concentration because the viscosity increase due to the presence of fibers.
Fig. 5a) Characteristic stress-strain curves from compressive test for non-coated, PVA-coated, PVA/5%MFC-coated and PVA/10%MFC coated scaffolds; b) Average compressive strength values of each set of samples with related scatters are summarized.

Characteristic tensile stress–strain curves for non-coated, PVA-coated, PVA/5%MFC-coated and PVA/10%MFC-coated scaffolds are shown in Fig. 6a. In the case of non-coated samples, the increase of load causes fracture of the first suitably oriented struts. However at this stage the load might be further increased until critical damage accumulation, i.e. when the critical loss of the bearing resistance of the struts is reached. This stage corresponds to simultaneous fracture of several struts/cells and sudden unstable drop of load. At this point, some few undamaged struts still exist and the load can be again increased until the onset of generalized fracture of the remaining cross-section occurs. Again, the coated ones do not exhibit any pop-in peaks at the initial stage of load increase and the first fracture events take place only at remarkably higher load in comparison with the non-coated samples.

For each set, seven samples were tested and average values with related scatters are reported in Fig. 6b. The average tensile strength value for uncoated scaffolds has been found to be $0.014 \pm 0.0031$ MPa. Samples coated by PVA exhibited more than 10 fold increase of tensile strength compared to non-coated samples, reaching an average value of $0.196 \pm 0.009$ MPa. The addition of 5 wt. % of MFC fibers into the coating led to a further increase up to $0.271 \pm 0.012$ MPa. However, the highest values were recorded for PVA/10%MFC-coated samples, whose average tensile strength reached $0.335 \pm 0.066$ MPa. PVA/10%MFC-coated samples exhibited larger scatter of results.
Fig. 6a) Characteristic stress–strain curves from tensile test for non-coated, PVA-coated, PVA/5%MFC-coated and PVA/10%MFC coated scaffolds, b) average tensile strength values of each set of samples with related scatters are summarized.

In Tab. 3 the values of elastic modulus measured by different techniques for uncoated, PVA-coated, PVA/5%MFC and PVA/10%MFC scaffolds are reported for the sake of comparison. For uncoated samples, the elastic modulus was estimated by using GA model (Eq. 1) and by calculating the slope of the elastic part of stress-strain curves. However, in the latter case, the values appear to be highly scattered (1 order of magnitude) and cannot be considered as reliable. On the other hand, coated specimens exhibited comparable values from both techniques. As expected, those calculated from the slope resulted as slightly lower, in agreement with the fact that the slope–approach generally underestimates the real stiffness. For the prediction of elastic modulus by GA model, $E_s$ has been set equal to 89 GPa (following section). Nevertheless it is possible to see that the presence of coating does not influence the stiffness of the structure, in agreement with Peroglio et al. [62].

<table>
<thead>
<tr>
<th>Method</th>
<th>No coating</th>
<th>PVA</th>
<th>PVA/5%MFC</th>
<th>PVA/10%MFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope of linear part</td>
<td>0.03 – 0.41</td>
<td>0.24</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>Resonance</td>
<td>-</td>
<td>0.25</td>
<td>0.30</td>
<td>0.29</td>
</tr>
<tr>
<td>GA model (Eq.10)</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

Tab. 3. Elastic modulus values (GPa) of uncoated and coated scaffolds, measured by different methods.

SEM images indicate that fibers are effective as load-bearing elements (Fig. 7). It is worth to point out that all the micrographs refer to specimens which have been deformed beyond their highest stress peak, in order to observe toughening mechanisms occurring in the plateau.
region. The occurrence of the crack bridging mechanism is evident in Fig. 7b–e and f, involving both the MFC and PVA. The fibrils spatial distribution along the crack front appears as optimal for the reinforcement purpose either considering the energy dissipation, arising from the fracture of single fibrils and the crack opening limitation effect. Despite that, fibrils can still supply effective reinforcing effect mainly in the final stage of specimen elongation. Fig. 7f shows a crack bridging carried out by MFC fibrils only, without extensive assistance of the PVA matrix. SEM observations of fracture surfaces of tensile samples therefore confirmed the beneficial effect of MFC addition for the improvement of the mechanical properties of porous brittle scaffolds.

Fig. 7a) Fracture morphology of broken struts of coated samples: PVA/5%MFC coated strut; b) detail of the PVA/MFC bridging in a PVA/5%MFC-coated specimen; c) struts fracture of
a PVA/10%MFC-coated specimen; d) detail of the coating at higher magnification; e) bridging by the PVA/MFC pack in PVA/5%MFC-coated specimen and f) bridging by MFC fibrils only PVA/10%MFC-coated specimen.

The model of a simplified two-dimensional cracked strut having rectangular shape and loaded in plane stress conditions has been created. Two different numerical simulations, evaluating the influence of coating stiffness and coating infiltration on $K_I$ and $\sigma_{22}$ were performed. For the first task, five parts were created: a non-coated strut; a strut with coating just on the surface, and struts having respectively 1/3, 2/3 and completely filled crack. For simplicity, the models were named as 1, 2, 3, 4 and 5 and they are represented in Fig. 8a.

The strut width ($W = 1$ mm), strut height ($h = 2$ mm), crack length ($a = 0.5$ mm) and crack tip radius ($\rho = 0.003$ mm) were used. The width of the ligaments was defined as $b = W-a$. For all models, the displacement was driven in small deformation and elastic regime. The stress intensity factor $K_I$ was determined via Contour integral with the option no degeneracy of elements at the crack tip (crack tip elements were all hexagonal shape) and using the criterion of maximum tangential stress. The Young modulus ($E_{PVA}$) and the Poisson’s ratio of PVA ($\nu_{PVA}$) were set as 4.1 GPa [63] and 0.46 [64], respectively. Then, the influence of $E_{PVA}$ on $K_I$ was also evaluated. For this purpose, a strut having same configuration as model 5 (PVA which penetrate until the crack tip) was considered and four simulations with increasing values of $E_{PVA}$ (3, 5, 6 and 7 GPa) were run. These models were named as 6, 7, 8 and 9 respectively. Such values of $E_{PVA}$ were chosen according to author’s previous investigation [65], and they were meant to be representative of PVA and PVA/MFC composite films having increasing stiffness.

![Fig. 8a) Definition of the FEM model used; b) and detail of the mesh at the crack tip.](image)

The modelled strut part was loaded by displacement, being constrained at the lower side and undergoing a displacement $\Delta y = +0.00017$ mm along Y direction on the top side (Fig. 8a). The element type CPS4R, featuring a 4-node bilinear plane stress quadrilateral with reduced integration and hourglass control was chosen (Fig. 8b). For each model, the computed $\sigma_{yy}$ values near the crack tip were compared to the stress singularity function (Eq. 4). The resulting mesh in the proximity of the crack tip is shown in Fig. 23b. The whole computational work, from the definition of the parts to the outputs calculation has been
accomplished by using the software Abaqus, v. 6-10. The results obtained from FEM are summarized in Tab. 4.

<table>
<thead>
<tr>
<th>Model</th>
<th>Description</th>
<th>$E_{PVA}$ (GPa)</th>
<th>$\sigma_{yy}$ (MPa)</th>
<th>$\sigma_{yy} \downarrow$ (%)</th>
<th>$K_I$ (MPa·m$^{1/2}$)</th>
<th>$K_I \downarrow$ (%)</th>
<th>$r_v$ (mm)</th>
<th>$r_v/b$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reference</td>
<td>4.1</td>
<td>19.62</td>
<td>-</td>
<td>3.71</td>
<td>-</td>
<td>0.500</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>Surface</td>
<td>4.1</td>
<td>18.14</td>
<td>7.5</td>
<td>3.54</td>
<td>4.6</td>
<td>0.500</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>1/3 filled crack</td>
<td>4.1</td>
<td>14.11</td>
<td>28.1</td>
<td>2.82</td>
<td>24.0</td>
<td>0.053</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>2/3 filled crack</td>
<td>4.1</td>
<td>10.38</td>
<td>47.1</td>
<td>2.13</td>
<td>42.6</td>
<td>0.035</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>3/3 filled crack</td>
<td>4.1</td>
<td>4.40</td>
<td>77.6</td>
<td>1.00</td>
<td>73.0</td>
<td>0.013</td>
<td>0.03</td>
</tr>
<tr>
<td>6</td>
<td>3/3 filled crack</td>
<td>3</td>
<td>4.74</td>
<td>75.8</td>
<td>1.07</td>
<td>71.2</td>
<td>0.014</td>
<td>0.03</td>
</tr>
<tr>
<td>7</td>
<td>3/3 filled crack</td>
<td>5</td>
<td>4.20</td>
<td>78.6</td>
<td>0.97</td>
<td>73.9</td>
<td>0.013</td>
<td>0.03</td>
</tr>
<tr>
<td>8</td>
<td>3/3 filled crack</td>
<td>6</td>
<td>4.04</td>
<td>79.4</td>
<td>0.94</td>
<td>74.7</td>
<td>0.012</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>3/3 filled crack</td>
<td>7</td>
<td>3.92</td>
<td>80.0</td>
<td>0.91</td>
<td>75.5</td>
<td>0.012</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Tab. 4. Description of different finite element models with related stress field distribution $\sigma_{22}$ and $K_I$.

The distance from the crack tip, in which the singularity function fits the computed $\sigma_{yy}$ distribution, has been defined as $r_v$ (Tab. 4) and it decreases as the depth of PVA infiltration increases. For model 1, assumed as the reference solution, $K_I$ resulted as equal to 3.71 MPa·m$^{1/2}$ and the computed $\sigma_{yy}$ values were accurately fitted by Eq. 5 along the whole ligament width ($r_v = b$).

Fig. 9. Two dimensional part, mesh and models used for FEM simulations with relative $\sigma_{22}$ distribution.

For Models 2-9, in which the crack geometry is modified by the presence of PVA, the stress fields at the crack tip are significantly influenced. It is interesting to point out that for model 2, where no wetting of crack surfaces occurs, the reduction of $K_I$ is almost negligible (5%) and $r_v \sim b$. As the PVA progressively penetrates into the crack, $K_I$ and $r_v$ decrease until reaching their minimum values for model 5 ($K_I \sim 1.0$ MPa·m$^{1/2}$ and $r_v \sim 0.02·b$). In this case
the reduction of $K_I$ in comparison with the reference model is 73%. The magnitude of $\sigma_{yy}$ distribution near the crack tip decreases as well with the increasing infiltration depth and it is shown in Fig. 9. As it is possible to notice from values reported in Tab.4, $\sigma_{yy}$ values at $r = 0.05 \text{ mm}$ ($\sigma_{yy}|_{0.05}$) are compared for all the studied models. The variation of $E_{\text{PVA}}$ (models 6-9) has only minor effect on $\sigma_{yy}$ at the crack tip and thus on $K_I$.

Since that, the parameters which determine the infiltration of a polymeric solution on a specific glass surface (i.e. wettability and viscosity) were then measured and then correlated to the results obtained from mechanical testing of the corresponding polymer-scaffold system (Fig. 10).

The addition of MFC to an aqueous PVA solution caused a decrease of the contact angle (Tab. 5). Because of the presence of $–\text{OH}$ groups, PVA has the capability of H-bonding with its solvents and decreases their surface tension as other surface active agents. In PVA aqueous solutions, both species, PVA (solute) and water molecules, are free to migrate and exert attractive forces of attraction on their immediate neighbours.

<table>
<thead>
<tr>
<th>Solution</th>
<th>PVA</th>
<th>PVA/5%MFC</th>
<th>PVA/10%MFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle</td>
<td>45.14 ± 0.66</td>
<td>34.02 ± 0.74</td>
<td>32.83 ± 1.67</td>
</tr>
</tbody>
</table>

*Tab. 5. Measured contact angles measured for PVA and PVA/MFC solutions on a Bioglass® substrate.*

In the bulk solution, PVA molecules remain at a higher free-energy state because of the large association tendency of water molecules among themselves through H-bond. Hence, PVA always has a tendency to migrate from bulk to the surface. The statistical accumulation in the surface of molecules with weaker fields results in a lowering of surface-free energy. The PVA solution analyzed in this work (0.02 g/mL) showed basically Newtonian behavior in a shear rate range from 0 to 400 1/s. Experimental data are in fact well fitted by a linear function ($m = 0.0043$, $R^2 = 0.999$). The PVA/5%MFC solution showed shear thinning behaviour from 0 up to 80 1/s. Data in this range are well fitted by the Herschel-Bulkely model ($\tau_0 = 0.0139$, $K = 0.0416$, $n = 0.7082$) and from 80 1/s onwards by a linear function having $m = 0.29$. PVA/10 MFC solution exhibited analogous behaviour, being fitted by Herschel-Bulkely model from 0 to 110 1/s ($\tau_0 = 0.0759$, $K = 0.0670$, $n = 0.6844$) and from 110 1/s onwards by a linear function having $m = 0.650$. The addition of MFC therefore resulted in an increase of viscosity as expected.
Fig. 10a) Characteristic stress vs. strain curves from tensile test for uncoated and coated scaffolds and b) $\sigma_{22}$ as a function of distance of the crack tip ($y=0$).

5.2. Bulk Bioglass® samples: sintering in oven vs. SPS

Vickers indent on a bulk Bioglass® surface sintered in conventional furnace can be observed in SEM micrographs shown in Fig. 11a. Palmqvist cracks departing from the corner are visible. At higher magnification (Fig. 11b) it possible to observe that nucleated crystals exert a crack deflection action but their distribution and size are such that an effective toughening cannot be achieved.

Young’s modulus resulted as 89 GPa, being in agreement with values reported by Hench et al. about partially crystallized 45S5Bioglass®. Bending strength values were ranging from 90.92 to 121.48 MPa, being in agreement with those reported by Filho et al. for crystallized 45S5 Bioglass® [21]. Indentation fracture toughness values were as well close to those reported by Nychka et al. who reported a value of $0.23 \pm 0.07$ MPa·m$^{1/2}$ for indentation loads higher than 0.35 N [19].
The density measured by Archimedes’ method was 2.53 ± 1.53 g/cm³, which corresponds to 95.53 % of Bioglass® theoretical density. Density values measured by image analysis of SEM micrographs resulted equal to 94.35 %, being in good agreement with those obtained from Archimedes’ method.

_Fig. 12. XRD pattern of Bioglass® powder compact sintered at 1050 °C for 1h_

Fig. 12 shows the XRD diffraction pattern obtained. The main crystallization phase detected was combeite high (Na₂CaSi₂O₆, PDF-2: Ref. code 98-002-1475). The secondary phase detected is rhenanite (NaCaPO₄, PDF-2: Ref. code 01-076-1456).

Concerning SPS, different sintering routes were tested, i.e. by extensively varying parameters such as sintering temperature (Tₛ), heating rate (hᵣ), holding time (tₕ), in order to establish the optimal conditions for the achievement of a dense and homogeneous microstructure. A first set of samples was produced and the processing parameters are summarized in Tab. 6. Sintering performed in absence of pressure at 1050°C led to samples with superior density (close to the theoretical) and Vickers hardness in comparison with those pressure-assisted. For samples Pre1-2 density and indentation Kᵦc values were slightly higher than the values measured for Bioglass® sintered in furnace. On the contrary, sample Pre9 which was sintered at 550°C, exhibited remarkably lower density and Kᵦc.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>T (°C)</th>
<th>t (min)</th>
<th>P (MPa)</th>
<th>H. r. (C/min)</th>
<th>d_rel (%)</th>
<th>HV 0.2 (–)</th>
<th>Kᵦc (MPa m¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre1</td>
<td>600</td>
<td>5</td>
<td>60</td>
<td>100</td>
<td>97.41</td>
<td>406.29 ± 18.18</td>
<td>0.47</td>
</tr>
<tr>
<td>Pre2</td>
<td>600</td>
<td>5</td>
<td>70</td>
<td>100</td>
<td>97.78</td>
<td>471.29 ± 20.75</td>
<td>0.49</td>
</tr>
<tr>
<td>Pre9</td>
<td>550</td>
<td>5</td>
<td>70</td>
<td>100</td>
<td>96.67</td>
<td>361.34 ± 21.42</td>
<td>0.25</td>
</tr>
<tr>
<td>PL6</td>
<td>1050</td>
<td>30</td>
<td>0</td>
<td>100</td>
<td>100.00</td>
<td>548.84 ± 38.51</td>
<td>-</td>
</tr>
<tr>
<td>PL8</td>
<td>1050</td>
<td>60</td>
<td>0</td>
<td>100</td>
<td>99.26</td>
<td>553.43 ± 32.95</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab. 6. _First set of SPS samples with related processing parameters and HV, Kᵦc measured values._
Samples sintered by SPS at 600°C/100 °Cmin\(^{-1}\)/70 MPa (Pre1-2-9) exhibited densities ranging from 96 to 97% of the theoretical one, being slightly lower than values reported by Grasso et al. (98.8 – 100%) [60]. A comparative assay of fracture toughness measured by indentation technique, revealed \(K_{IC}\) values nearly 60 % than Bioglass\(^{\circledR}\) sintered by conventional method. In the case of samples sintered at 550 °C/70 MPa for 30 min, the density and \(K_{IC}\) resulted considerably lower than those sintered in oven, being 2.61 g/cm\(^3\) and to 0.25 MPa·m\(^{1/2}\), respectively. For samples Pre1-2-9, similar configuration of cracks was observed. Palmqvist cracks depart from the indents corners, similarly to samples sintered by conventional furnace. The length and shape of the cracks is comparable as well (20 < c < 50 μm).

The pressureless sintering, even if performed at temperatures above \(T_g\) and for much longer time, led to a much finer microstructure and density very close to theoretical one. The absence of detectable pores from SEM pictures is consistent with the material being theoretically dense. SEM observation revealed crystalline and amorphous phases as tightly interlocked at sub-micrometric scale. Even at higher magnification it resulted very hard to clearly distinguish the crystalline domains from the amorphous matrix.

For the second set of samples, all the related sintering parameters are summarized in Tab. 7.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(H_r) (°C/min)</th>
<th>(T_s) (°C)</th>
<th>(t) (min)</th>
<th>(P) (MPa)</th>
<th>(d) (g/cm(^3))</th>
<th>(d_{rel}) (%)</th>
<th>(K_{IC}) (MPa·m(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB01</td>
<td>100</td>
<td>1050</td>
<td>30</td>
<td>vacuum</td>
<td>2.7</td>
<td>100.00</td>
<td>1.05 ± 0.05</td>
</tr>
<tr>
<td>PB02</td>
<td>300</td>
<td>1050</td>
<td>30</td>
<td>vacuum</td>
<td>2.68</td>
<td>99.25</td>
<td>1.23 ± 0.21</td>
</tr>
<tr>
<td>PB03</td>
<td>100</td>
<td>1000</td>
<td>20</td>
<td>vacuum</td>
<td>2.64</td>
<td>97.77</td>
<td>0.89 ± 0.03</td>
</tr>
<tr>
<td>PB05</td>
<td>300</td>
<td>1000</td>
<td>30</td>
<td>vacuum</td>
<td>2.65</td>
<td>98.14</td>
<td>0.84 ± 0.16</td>
</tr>
<tr>
<td>PB06</td>
<td>100</td>
<td>1050</td>
<td>30</td>
<td>vacuum</td>
<td>2.68</td>
<td>99.25</td>
<td>1.01 ± 0.17</td>
</tr>
<tr>
<td>PB07</td>
<td>100</td>
<td>1050</td>
<td>30</td>
<td>vacuum</td>
<td>2.70</td>
<td>100.00</td>
<td>1.4 ± 0.11</td>
</tr>
<tr>
<td>PB08</td>
<td>100</td>
<td>1050</td>
<td>60</td>
<td>vacuum</td>
<td>2.67</td>
<td>98.88</td>
<td>1.5 ± 0.10</td>
</tr>
</tbody>
</table>

Tab. 7. Second set of SPS samples with related processing parameters and, \(K_{IC}\) values.

XRD diffraction patterns obtained for PB01 PB02, PB08 and Bioglass\(^{\circledR}\) sintered by conventional method are shown in Fig. 13.
For the second set of samples, $K_{IC}$ was measured by Chevron technique. Values were found to be from 3 to 5 times higher than oven-sintered Bioglass reaching the maximum values for PB07 and PB08 (respectively $1.4 \pm 0.11$ and $1.5 \pm 0.10$ MPa-m$^{1/2}$). Toughening could be ascribed to a finer and interpenetrated structure (Fig. 14). Abe et al. [66] demonstrated that a glass-ceramics that features an interlocking crystal microstructure exhibit the highest toughness. Beside the spatial distribution of amorphous and crystalline phase, it should be taken into account the orientation of nucleated crystals.

Moreover it was possible to observe domains oriented along a defined direction and departing from the indent corners (Fig. 14b). The propagated cracks seemed to undergo a healing process which led to their complete closure. This represents a very interesting phenomenon which has not been reported yet for the 45S5 composition. Non-equilibrium phases might originate pursuant to rapid heating/cooling and recrystallize consequently to the mechanical interaction between the indenter tip and the specimen surface. Another influencing factor could be the atmosphere (vacuum in this case). Although the relationships between the several polymorphisms of silica and silica-based glasses and sintering temperature are well known, the effect of sintering atmosphere and high heating/cooling rates on the crystallization behaviour of silica glass has been poorly described yet. What it has been assessed is that, the composition of the sintering atmosphere and the partial pressure of its constituent influences the diffusivity in the sintering material as well as the densification kinetics, grain growth, phase stability and stoichiometry [57].
Fig. 14a, b) Vickers indent at 1.96 N on Pre6 observed one week after test. Transformation and healing seems to occur in correspondence of the crack path. Cracking and debonding at the interface of the two phases were observed as well (c, d, e).

In order to determine the kinetic of the phase transformation, the indent morphology was reconstructed by confocal microscope immediately after the indentation and after 24 h. The images are compared in Fig. 15. As it visible, a change of indent topography occurs. Moreover the area surrounding the indent appears as remarkably protruded, consequently to volumetric expansion. One likely hypothesis could be that the deformation energy which remains stored inside the material at the cracks proximity is spent into the transform from a metastable to a stable phase. Hence, even if it has not been determined what occurs instantaneously in the matrix as the crack propagates, it is possible to observe that phase transformation is time-dependent.
Fig. 15a) 3D reconstruction of the indent profile straight after indentation; b) 24 hours after the indentation with related 2D profiles.
6. Conclusions

1. Results from FE modelling demonstrated that the dominant criterion for the strengthening for polymer-coated scaffolds is the extent of coating infiltration into surface cracks, which is maximized as the polymer reaches the crack tip. As the polymer reaches the crack tip, the highest reduction of $K_I$ and $\sigma_{yy}$ is achieved. It is therefore crucial to optimize the wettability and viscosity of polymeric solutions designed for dip-coating (i.e. the choice of a suitable polymer-solvent system and polymer concentration) in order to maximize the infiltration capability into the surface defects.

2. The presence of fibres determines a consistent increase of viscosity in the system. Thus, a balance between these two effects must be achieved.

3. SEM observations revealed a homogeneous distribution of the coating on the struts surface and a sufficiently strong interface to guarantee stress transfer from the struts to the coating. PVA provides the load transfer from the scaffold to the MFC. In addition, fracture of MFC fibers contributed to the energy dissipation process which led to the increase of the toughness of the scaffolds.

4. Ethanol-based slurry has been adopted for the first time for the production of 45S5 Bioglass® scaffolds. Resulting scaffolds exhibited 3D interconnected structure with higher degree of open porosity in comparison with water-based Bioglass® slurries commonly reported in literature.

5. DTA revealed two crystallization peaks at approximately 600 and 810 °C respectively. The latter crystallization peak was associated with the crystallization of $\beta$-NaCa(PO$_4$) ($\beta$-rhenanite). The spectrum of $\beta$-rhenanite better fitted the experimental spectrum in comparison with silico-rhenanite, which was previously reported by Lefebvre et al.

6. PVA-coated samples exhibited approximately 5 fold increase of compressive strength compared to uncoated ones and the addition of 5 wt% of MFC fibers led to a 10 fold increase of compressive strength. Also tensile strength has been found to be improved by the PVA/MFC composite coating; the PVA/10%MFC-coated samples exhibited more than 20 fold increase of tensile strength compared to non-coated samples.

7. SPS performed in absence of mechanical pressure and at heating rates ranging from 100 to 300 °C/min enabled the production of samples having theoretical density and fracture toughness nearly 4 times higher in comparison with conventional sintering. Crack deflection was established as the main toughening mechanisms were detected.

8. Time–dependent crack healing process at room temperature was observed as well and further investigation is required. As explanation for the latter phenomenon, the author postulates that crystallization of a glassy metastable phase might occur pursuant to the release of strain energy stored in the material after indent.
References


List of publications related to thesis

International conferences

- **Luca Bertolla**, Ivo Dlouhý, Řehořek, Zdeněk Chlup. Tensile properties of open cell ceramic foams. E-MRS 2012 fall meeting, September 17-21, Warsaw, Poland (poster).

Journals

Summary

Bioactive glasses exhibit unique characteristics as a scaffold material for bone tissue engineering. Unfortunately, its extensive application for the repair of load-bearing bone defects is still limited by low mechanical strength and fracture toughness. The main aim of this work was two-fold: the reinforcement of brittle Bioglass®-based porous scaffolds and the production of bulk Bioglass® samples exhibiting enhanced mechanical properties. For the first task, scaffolds were coated by composite coating constituted by polyvinyl alcohol (PVA) and microfibrillated cellulose (MFC). Scaffolds were produced by foam replication process, using a novel ethanol-based Bioglass® slurry. The addition of PVA/MFC coating led to a 10 fold increase of compressive strength and a 20 fold increase of tensile strength in comparison with non-coated scaffolds. SEM observations of broken struts surfaces proved the reinforcing and toughening effect of the composite coating which was ascribed to crack bridging and fracture of cellulose fibrils. The mechanical properties of the coating material were investigated by tensile testing of PVA/MFC stand-alone specimens. The stirring time of the PVA/MFC solution came out as a crucial parameter in order to achieve a more homogeneous dispersion of the fibers and therefore enhanced strength and stiffness. A simplified two-dimensional finite elements model was created for a PVA-coated Bioglass® strut undergoing tensile stresses (loading mode I). The infiltration of the coating until the crack tip resulted as the most effective criterion for the struts strengthening. Contact angle and linear viscosity measurements of PVA/MFC solutions showed that MFC causes a reduction in θ and a drastic increase in η, indicating that a balance between these two effects must be achieved. Concerning the production of bulk samples, spark plasma technique (SPS) was used. Sintering performed in absence of mechanical pressure and at heating rates ranging from 100 to 300 °C/min enabled the production of samples having theoretical density and KIC nearly 4 times higher in comparison with conventional sintering. SEM analysis on Vickers indent revealed crack deflection as the main toughening mechanisms. Time-dependent crack healing process was observed as well and further investigation on the non-equilibrium phases crystallized is required.